CASE WESTERN RESERVE UNIVERSITY EST. 1826

Office of Research Administration
10900 Euclid Avenue
Cleveland, Ohio 44106-7037
phone 216.368.5939
fax 216.368.4679

March 1, 2017

Defense Technical Information Center
8725 John J Kingman Road, Suite 0944
Fort Belvoir, VA 22060-6218

To Whom it May Concern:

Please find enclosed the Final Technical Report and SF 298 for N00173-12-2-C001 for your records. Feel free to contact me directly should you need anything further during the closeout process of this award.

Sincerely,

Karen Dunn
Assistant Director, Pre-award Services

Interstitial Hardening of Stainless Steel for Enhanced Corrosion Resistance for Naval Applications

Final Report (Contract NOO173-12-2-C001)

Collaborative work between the Corrosion Science group at NRL and the Dept. of Materials Science and Engineering at CWRU had demonstrated that a novel low temperatures "paraequilibrium" interstitial hardening process led to a dramatic improvement in corrosion resistance of austenitic stainless steels in marine environments. This prior work had been concerned with carburization, mostly using carbon monoxide (CO) as the carbon source. Inasmuch as many commercial hardening processes involve nitridation or nitrocarburization, one of the principal aims of the program was to establish whether interstitial hardening treatments using nitrogen in isolation, or in combination with carbon, could likewise enhance corrosion resistance of austenitic stainless steels, and if so, to define the optimum treatment conditions.

Hardened corrosion-resistant "cases" could be achieved with nitrogen alone or in combination with carbon, but there were interesting differences compared to carbon alone. In particular, a larger surface nitrogen content and greater surface hardening, could be achieved at high chemical activities of nitrogen (achieved by using ammonia (NH_3) as the nitrogen source) but this led to severe surface cracking. Fortunately, it is straightforward to nitride at lower nitrogen activities by mixing NH_3 with hydrogen (H_2) gas and a systematic study of nitridation was conducted at various nitrogen activities. These studies also revealed that austenite of 316 composition (18% Cr, 12% Ni) became ferromagnetic when the nitrogen content exceeded 14 at %. Early theoretical work had predicted that when the lattice parameter of face centered cubic (fcc) iron (e.g. austenite) was expanded, a paramagnetic to ferromagnetic transition should occur. The nitridation studies revealed substantial lattice panameter expansion and confirmed that expanded austenite could indeed become ferromagnetic. This has implications for naval applications of interstitially hardened austenite, which may not be sufficiently magnetically "quiet".

Nitrocarburnizing using either NH_3/ CH_4 (methane) mixtures or gaseous usea (CH_4N_2O) was also conducted. Simultaneous and sequential nitro-carburization (nitriding followed by carburizing or carburizing followed by nitriding) was studied. Characterization of the interstitial depth profiles using scanning Auger spectroscopy revealed the non-intuitive finding that carbon enters the austenite lattice to a greater depth than does nitrogen, regardless of whether nitridation proceeds or follows carburization, or if both interstitial solutes enter the austenite lattice simultaneously. A straightforward thermodynamically based numerical model was developed that explained "simple" carburization and nitridation depth profiles, and also explained the deeper carbon profiles, based on the effects of carbon on the chemical potential of nitrogen in the steel and vice versa.

Other significant findings included orientation-dependent depth profiles developed during nitridation, and successful nitrocarburization using urea as the source for both carbon and nitrogen interstitials. Essentially all these findings have been reported in top-ranked archival technical journals.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
12/01/2016

2. REPORT TYPE
FINAL

3. DATES COVERED *(From - To)*
1/1/12-9/30/16

4. TITLE AND SUBTITLE
Interstitial Hardening of Stainless Steel for enhanced corrosion resistance for naval applications.

5a. CONTRACT NUMBER
N00173 12-2-C001

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHOR(S)
DR. ARTHUR HEUER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
CASE WESTERN RESERVE UNIVERSITY
10900 EUCLID AVE.
CLEVELAND, OHIO 44106-7015

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
NAVAL RESEARCH LABORATORY
4555 OVERLOOK AVE. SW
WASHINGTON, DC 20375

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
APPROVED FOR PUBLIC RELEASE, DISTRIBUTION IS UNLIMITED

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Low temperature interstitial hardening using nitrogen alone or in combination with carbon was shown to be effective in improving the corrosion resistance of austenitic stainless steels in marine environments, although there were interesting differences from the more familiar carburization. In particular, higher surface nitrogen concentrations (and greater surface hardness) could be achieved but was accompanied by surface micro-cracking; this undesirable aspect could be avoided by nitriding using a lower nitrogen chemical activity. Nitro-carburizing led to a two-zone hardened "case", as carbon entered the austenite lattice to a greater depth than did nitrogen, regardless of whether nitrogen preceded or followed carburization.

15. SUBJECT TERMS
Corrosion Processes: Control and Mitigation.

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON / 19b. TELEPHONE NUMBER *(Include area code)*
U	U	U	UU		